Role of External Flow and Frame Invariance in Stochastic Thermodynamics

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For configurational changes of soft matter systems affected or caused by external hydrodynamic flow, we identify applied work, exchanged heat, and entropy change on the level of a single trajectory. These expressions guarantee invariance of stochastic thermodynamics under a change of frame of reference. As criterion for equilibrium *vs.* nonequilibrium, zero *vs.* nonzero applied work replaces detailed balance *vs.* nonvanishing currents, since both latter criteria are shown to depend on the frame of reference. Our results are illustrated quantitatively by calculating the large deviation function for the entropy production of a dumbbell in shear flow.

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Thermodynamic notions like applied work, dissipated heat, and entropy have been used successfully to analyze processes in which single colloidal particles or biomolecules are manipulated externally [1]. Various exact relations have been shown to constrain the distribution function arising from the ever present thermal fluctuations on this scale [2, 3, 4, 5]. So far, the systematic conceptual work has been focused on cases where the driving crucial to generate a nonequilibrium situation arises from a time-dependent potential expressing the effect of a moving laser trap, micropipet, or AFM tip. In these cases, the identification of external work, internal energy and hence dissipated heat is straightforward. Many experiments on a variety of systems have proven the consistency and potency of such an extension of thermodynamic notions to the micro or nano world [6, 7, 8, 9, 10, 11].

As another source of nonequilibrium, external hydrodynamic flow arguably is the most common and best studied case in soft matter systems. On the level of single objects like a polymer, vesicle, or red-blood cell, it can cause dramatic shape transitions (for recent examples see, e.g., Refs. [12, 13, 14, 15, 16]). The theoretical analysis of these phenomena is typically based on equations of motion like the Langevin equation for single objects or distribution functions and their projection to few-body correlation functions for bulk systems like colloidal suspensions [17, 18, 19]. Concepts like work or entropy production, however, have played no systematic role in describing such phenomena yet. Having in mind the conceptual advantage achieved for time-dependent potentials by using such notions, the question arises quite naturally whether a similar analysis for nonequilibrium phenomena in soft matter systems caused by external flow is possible. Indeed, Turitsyn *et al.* [20] calculated the entropy production for linear equations of motion and illustrated it for a dumbbell in shear flow. However, their identification of entropy production was not related to the dissipated heat leading to a fundamentally different dependence on the external flow.

Conceptually, there is an even deeper issue hidden behind the proper treatment of external flow. Its presence or absence depends on the frame of reference as the presence or absence of currents does. Since the latter are usually taken as an indicator for nonequilibrium, our analysis will question the traditional role of both detailed balance and nonvanishing currents as criteria for equilibrium and nonequilibrium, respectively. They will be replaced by a frame-independent identification of applied work.

For an almost trivial but revealing paradigmatic case, consider a colloidal particle dragged through a viscous fluid along the trajectory $x(t)$ by a harmonic laser trap of strength k moving with velocity u_0 [6, 8]. In the laboratory frame, the particle is moving in a time-dependent potential $U(x,t) = (k/2)(x-u_0t)^2$. By applying the standard definition of work [2] as the external change of the potential energy, the applied power

$$\dot{w} = \partial_t U \tag{1}$$

becomes $\dot{w} = -u_0k(x-u_0t)$. Changing to the comoving frame with $y \equiv x - u_0t$, the potential $U(y) = (k/2)y^2$ becomes time-independent and therefore one would naively find $\dot{w} = 0$. Of course, the work should be independent of the chosen frame of reference. Moreover, since in the comoving frame detailed balance holds and no current in the y variable occurs, one would usually consider the system to be in equilibrium in this representation. The physical origin of the apparent contradictions is the fact that in the comoving frame the particle experiences a steady flow of the fluid with velocity $-u_0$. Due to friction, this flow pushes the particle against the force of the potential thus spending work. The standard definition of work fails in the presence of flow since the flow advects the particle, which is not accounted for in Eq. (1). Modifying this expression will affect also the expression for the heat dissipated into the fluid as well as the expression for the entropy production.

We will now derive the refined expressions for work and heat in the presence of a, possibly time-dependent, external flow $\mathbf{u}(\mathbf{r},t)$. For complete generality and future applications, we consider a soft matter system like polymers, membranes, or a colloidal suspension composed of N particles with positions $\Gamma \equiv \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$. The index denotes the particle number and in the following we sum over same indices. The system has a total energy $U(\Gamma,t)$

which is the sum of an internal energy due to particle interactions and a possible contribution due to external potentials. In addition to direct interactions, we allow for hydrodynamic interactions which are of great importance for soft matter systems.

In 1997, Sekimoto formulated the first law of thermodynamics $\delta q = \delta w - \mathrm{d}U$ along a single stochastic trajectory [21]. We follow this route and start by identifying three possible sources of work w, i.e., of changes of energy caused externally. First, the potential energy $U(\Gamma, t)$ can be time-dependent if it is manipulated externally. Second, it is convenient to allow for direct nonconservative forces $\mathbf{f}_k$ that spend work through displacing the particles. Third, the external flow drives the system and therefore changes its energy, which must be taken into account as work as well. The advection of particles is described through the convective derivative $\mathrm{D}_t \equiv \partial_t + \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k$. Through both replacing the partial derivative in Eq. (1) with the convective derivative and measuring particle displacements with respect to the flow, we obtain the new definition

$$\dot{w} \equiv \mathrm{D}_t U + \mathbf{f}_k \cdot [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \tag{2}$$

for the work increment $\delta w = \dot{w}\mathrm{d}t$ which replaces Eq. (1). The first law then leads to the heat production rate

$$\dot{q} \equiv \dot{w} - \mathrm{d}U/\mathrm{d}t = [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot [-\nabla_k U + \mathbf{f}_k]. \tag{3}$$

The sign of heat is convention, here we take it to be positive if energy is dissipated into the surrounding fluid. The expression (3) shows that no heat is dissipated when particles move along a fluid trajectory, $\dot{\mathbf{r}}_k = \mathbf{u}(\mathbf{r}_k)$. In this case, the applied work corresponds to the change in total energy.

A change of frame necessarily changes the flow therefore leaving the expressions for work (2) and heat (3) invariant. Explicitly, we can allow time-dependent orthogonal transformations and an arbitrary time-dependent shift of the origin. Coming back to the introductory example, we see that for a stationary trap in the comoving frame with flow $u = -u_0$, the applied power following Eq. (2) now reads $\dot{w} = -u_0 k y$ in agreement with the rate obtained for a moving trap and resting fluid. Finally, note that the definitions (2) and (3) are independent of whether or not hydrodynamic interactions are induced. These will affect the dynamics but they do not enter the definitions of work and heat explicitly.

We now turn to entropy production. A trajectory dependent stochastic entropy is defined as $s(t) \equiv -\ln \psi(\Gamma(t), t)$ through the distribution function $\psi(\Gamma, t)$ of the N particle positions [5]. The temperature of the surrounding fluid is T and throughout the paper, we set Boltzmann's constant to unity. Calculating the total time derivative $\dot{s} \equiv \mathrm{d}s/\mathrm{d}t$, we obtain the equation of motion

$$\begin{aligned} \dot{s} = \partial_t s - \dot{\mathbf{r}}_k \cdot \nabla_k \ln \psi = \mathrm{D}_t s + [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \boldsymbol{\mathcal{F}}_k / T \\ - [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot [-\nabla_k U + \mathbf{f}_k]/T, \end{aligned} \tag{4}$$

where we have separated the heat production rate (3) and introduced the total effective force

$$\boldsymbol{\mathcal{F}}_k \equiv -\nabla_k (U + T \ln \psi) + \mathbf{f}_k. \tag{5}$$

Apart from the gradient of the potential energy $U(\Gamma, t)$ and nonconservative forces $\mathbf{f}_k$ that cannot be written as gradient of a potential, a "thermodynamic" force contributes to $\boldsymbol{\mathcal{F}}_k$ arising from the stochastic interactions between system and the surrounding fluid [17]. In the absence of external flows and nonconservative forces, detailed balance must hold. The thermodynamic force then ensures that $\nabla_k (U + T \ln \psi) = 0$ leads to the correct Gibbs-Boltzmann equilibrium distribution $\psi_{\mathrm{eq}} \sim \exp(-U/T)$. In Eq. (4), the last term is the heat (3) divided by the temperature of the fluid T. We interpret this term as the entropy produced in the fluid through Clausius' formula $\Delta s_{\mathrm{m}} = q/T$. The total entropy production rate $\dot{s}_{\mathrm{tot}} \equiv \dot{s} + \dot{s}_{\mathrm{m}}$ then becomes

$$\dot{s}_{\mathrm{tot}} = \mathrm{D}_t s + [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \boldsymbol{\mathcal{F}}_k / T. \tag{6}$$

The mean total entropy production rate follows as

$$T \langle \dot{s}_{\mathrm{tot}} \rangle = \langle [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \boldsymbol{\mathcal{F}}_k \rangle \tag{7}$$

since the mean of the convective derivative is zero for incompressible fluids ($\nabla \cdot \mathbf{u} = 0$) and vanishing boundary terms.

So far we did not resort to a specific dynamics. However, in order to both prove positivity of Eq. (7) and give it a more familiar appearance known from the theory of polymer dynamics [17], we turn to the Smoluchowski equation [17, 18]

$$\partial_t \psi + \nabla_k \cdot (\mathbf{v}_k \psi) = 0 \tag{8}$$

governing the evolution of the distribution function $\psi(\Gamma, t)$. Any deviation of a particle's local mean velocity

$$\mathbf{v}_k \equiv \mathbf{u}(\mathbf{r}_k) + \boldsymbol{\mu}_{kl} \boldsymbol{\mathcal{F}}_l \tag{9}$$

from the velocity of the external flow $\mathbf{u}(\mathbf{r})$, which drags the particles due to friction, has to be caused by the total force $\boldsymbol{\mathcal{F}}_k$. In this model, hydrodynamic interactions now enter through a dependence of the symmetric mobility matrices $\boldsymbol{\mu}_{kl}(\Gamma)$ on the particle positions Γ. We demand the inverse matrices defined through $\boldsymbol{\mu}_{km} \boldsymbol{\mu}^{-1}_{ml} = \mathbf{1}\delta_{kl}$ to exist. Specific expressions for $\boldsymbol{\mu}_{kl}$ are obtained from either the Oseen or Rotne-Prager tensor [18].

The local mean velocity $\mathbf{v}_k(\Gamma, t)$ is the average of the actual stochastic velocity $\dot{\mathbf{r}}_k$ over the subset of trajectories passing through a given configuration Γ. This allows

us to perform the mean in Eq. (7) in two steps: First, we average over stochastic trajectories crossing a specific point Γ in configuration space, which amounts to replacing $\dot{\mathbf{r}}_k$ by $\mathbf{v}_k$. Second, we average over the distribution $\psi(\Gamma, t)$ of the point Γ. Finally, we use Eq. (9) to replace the total force $\boldsymbol{\mathcal{F}}_k$. The resulting quadratic expression

$$T\langle \dot{s}_{\rm tot} \rangle = \langle [\mathbf{v}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \boldsymbol{\mu}_{kl}^{-1} [\mathbf{v}_l - \mathbf{u}(\mathbf{r}_l)] \rangle \geqslant 0 \tag{10}$$

is well known phenomenologically as the energy dissipation function in the theory of polymer dynamics [17]. It is nonnegative with the equal sign holding in equilibrium only where $\boldsymbol{\mathcal{F}}_k = 0$.

On the trajectory level, we have identified heat and entropy production using physical arguments. There is a more formal way of identifying entropy by starting from the weight $P[\Gamma(t)|\Gamma_0] \sim \exp\{-S[\Gamma(t)|\Gamma_0]/T\}$ for a trajectory $\Gamma(t)$ starting in $\Gamma(0) = \Gamma_0$ involving the action S. The entropy produced in the surrounding medium is usually identified with the part of the action that is asymmetric with respect to time-reversal [22]. For explicit expressions for both the path probability and the action in the presence of hydrodynamic interactions as needed in our case, we refer to Ref. [23].

We can deduce two expressions for the asymmetric part of the action since in the presence of external flow, we have two choices how to define the operation "time reversal". First, we could formally treat the flow as a nonconservative force. It would then be invariant with respect to time reversal and we would obtain

$$\dot{s}_{\rm m}^* = \dot{\mathbf{r}}_k \cdot [-\nabla_k U + \mathbf{f}_k + \boldsymbol{\mu}_{kl}^{-1} \mathbf{u}(\mathbf{r}_l)]/T. \tag{11}$$

This expression has been identified with the entropy production rate in Ref. [20]. Second, we can extend the operation of time reversal to the particles of the fluid, which is physically more appropriate. Reversing the velocity of the fluid particles then effectively amounts to the change of the sign of the external flow velocity $\mathbf{u}(\mathbf{r})$. This leads to $\dot{s}_{\rm m} = \dot{q}/T$ involving the heat production rate from Eq. (3). We thus recover the physically motivated definition of the heat (3) as the asymmetric part of the action under time reversal only if the flow is reversed as well [20].

For a discussion of the crucial difference between Eqs. (11) and (3) in a specific system, consider a dumbbell in a flow $\mathbf{u}(\mathbf{r}) = \boldsymbol{\kappa}\mathbf{r}$ with traceless matrix $\boldsymbol{\kappa} = \boldsymbol{\kappa}^{\rm S} + \boldsymbol{\kappa}^{\rm A}$, which can be split up into a symmetric part $\boldsymbol{\kappa}^{\rm S}$ and a skew-symmetric part $\boldsymbol{\kappa}^{\rm A}$. The dumbbell consists of two particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ with displacement $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$ and potential energy $U(\mathbf{r}) = (k/2)\mathbf{r}^2$. The applied power (2) then becomes

$$\dot{w} = \mathbf{u}(\mathbf{r}) \cdot \nabla U = k\mathbf{r} \cdot \boldsymbol{\kappa}^{\rm S} \mathbf{r}, \tag{12}$$

i.e., only the symmetric part $\boldsymbol{\kappa}^{\rm S}$, which reflects an elongation flow component, contributes to the work. Physically, the elongation flow drags the two particles apart due to friction and therefore spends permanently work against the elastic force keeping the particles together. Neglecting the boundary term $\Delta U/t \sim 0$ in the long time limit, the time-extensive part of the entropy production rate is then $\dot{s}_{\rm m} \sim (k/T)\mathbf{r} \cdot \boldsymbol{\kappa}^{\rm S}\mathbf{r}$. Note that here only the displacement $\mathbf{r}$ enters. This is not true if the expression (11) is interpreted as entropy production rate, leading to the time extensive part

$$\dot{s}_{\rm m}^* \sim (T\mu_0)^{-1} [2\dot{\mathbf{R}} \cdot \boldsymbol{\kappa}^{\rm A} \mathbf{R} + (1/2)\dot{\mathbf{r}} \cdot \boldsymbol{\kappa}^{\rm A} \mathbf{r}] \tag{13}$$

with bare mobility μ_0. Here, also the center of mass $\mathbf{R} \equiv (\mathbf{r}_1 + \mathbf{r}_2)/2$ contributes. This is obviously physically unsound as the center of mass undergoes free diffusion and therefore does not produce entropy in the medium on average. Moreover, even in the second term of Eq. (13) concerning the relative motion, the source of dissipation is the skew-symmetric part $\boldsymbol{\kappa}^{\rm A}$ in contrast to Eq. (12).

We will now calculate the large deviation function of the medium entropy production rate for the dumbbell in two-dimensional shear flow, i.e., all entries of the matrix $\boldsymbol{\kappa}$ are now zero except $\kappa_{xy} = \dot{\gamma}$ where $\dot{\gamma}$ is the strain rate [18]. The large deviation function

$$h(\sigma) \equiv \lim_{t\to\infty} -\frac{1}{t} \ln p(\Delta s_{\rm m}, t) \tag{14}$$

quantifies the asymptotic fluctuations $\sigma = \Delta s_{\rm m}/(\langle \dot{s}_{\rm m} \rangle t)$ of the entropy production in the limit of large observation times t with mean production rate $\langle \dot{s}_{\rm m} \rangle$. Instead of obtaining the function $h(\sigma)$ from the time-dependent probability distribution $p(\Delta s_{\rm m}, t)$ directly, we will calculate its Legendre transform $\alpha_0(\lambda)$ as the lowest eigenvalue of the operator $\hat{L}_\lambda = \hat{L}_0 - \lambda \dot{s}_{\rm m}$. The operator $\hat{L}_\lambda$ governs the evolution of the generating function [24, 25, 26]. The production rate depends only on the displacement $\mathbf{r}$, whose dynamics is determined through the Smoluchowski operator [17] $\hat{L}_0 = \tau_0^{-1} \nabla \cdot [\mathbf{r} + (T/k)\nabla] - \boldsymbol{\kappa}\mathbf{r} \cdot \nabla$. For this illustration, we neglect hydrodynamic interactions by using mobility matrices $\boldsymbol{\mu}_{kl} = \mu_0 \mathbf{1} \delta_{kl}$ defining the time scale $\tau_0^{-1} \equiv 2\mu_0 k$.

For the lowest eigenfunction of the eigenvalue equation

$$\hat{L}_\lambda \psi_0(\mathbf{r}, \lambda) = -\alpha_0(\lambda)\psi_0(\mathbf{r}, \lambda), \tag{15}$$

we use the ansatz $\psi_0 = \exp[-(k/2T)\mathbf{r} \cdot \mathbf{C}_\lambda \mathbf{r}]$ with a symmetric matrix $\mathbf{C}_\lambda$. We are lead to this ansatz since we know that the stationary distribution ($\lambda = 0$) of $\mathbf{r}$ is a Gaussian [27], where $\mathbf{C}_0$ becomes the inverse covariance matrix. Inserting this ansatz into Eq.(15) results in $\alpha_0(\lambda) = \tau_0^{-1} \,\mathrm{tr}(\mathbf{C}_\lambda - \mathbf{1})$, where $\mathbf{C}_\lambda$ is the solution of the quadratic matrix equation

$$(\mathbf{C}_\lambda + \mathbf{D})^{\rm T} (\mathbf{C}_\lambda + \mathbf{D}) = \mathbf{S}_\lambda,$$

$$\mathbf{S}_\lambda = \frac{1}{4} \begin{pmatrix} 1 & \tilde{\gamma}(2\lambda - 1) \\ \tilde{\gamma}(2\lambda - 1) & 1 + \tilde{\gamma}^2 \end{pmatrix}, \quad \mathbf{D} = \frac{1}{2} \begin{pmatrix} -1 & \tilde{\gamma} \\ 0 & -1 \end{pmatrix}.$$

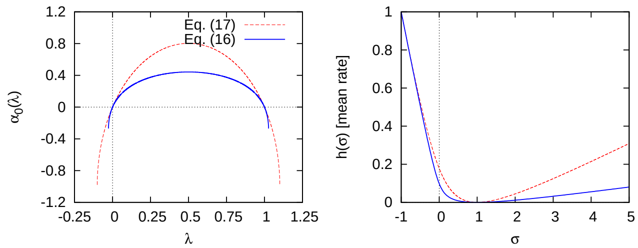

FIG. 1: Left: Comparison of the eigenvalue $\alpha_0(\lambda)$ from Eq. (16) (solid) with the solution (17) obtained in Ref. [20] (dashed) based on Eq. (11). (Parameters for both curves are $\tilde{\gamma} = 3$ and $\tau_0 = 1$.) The mean entropy production rate is the same for both expressions as indicated by the matching slope at $\lambda = 0$. Right: The corresponding large deviation functions $h(\sigma)$ obtained from the Legendre transform of $\alpha_0(\lambda)$.

The only parameter left is the dimensionless strain rate $\tilde{\gamma} \equiv \dot{\gamma}\tau_0$. We only need the trace of the matrix $\mathbf{C}_\lambda$, which, after some tedious calculations, can be expressed as

$$\operatorname{tr}\mathbf{C}_\lambda = \sqrt{\operatorname{tr}\mathbf{S}_\lambda + 2\sqrt{\det\mathbf{S}_\lambda} - \tilde{\gamma}^2/4} - \operatorname{tr}\mathbf{D}$$

leading to the solution

$$\alpha_0(\lambda) = \tau_0^{-1}\left[\sqrt{\tfrac{1}{2} + \tfrac{1}{2}\sqrt{1 + 4\tilde{\gamma}^2\lambda(1-\lambda)}} - 1\right]. \qquad (16)$$

This function is defined within the interval $\lambda_- \leqslant \lambda \leqslant \lambda_+$ with branch points $\lambda_\pm = \frac{1}{2}(1 \pm \sqrt{1 + \tilde{\gamma}^{-2}})$. Such branch points imply linear asymptotes for $h(\sigma)$ and therefore exponential tails for the distribution $p(\Delta s_\mathrm{m})$ [31]. On the level of the function $\alpha_0(\lambda)$, the fluctuation theorem [5, 24, 28, 29] is expressed through the symmetry $\alpha_0(\lambda) = \alpha_0(1-\lambda)$, which is fulfilled by Eq. (16). In Fig. 1, we compare the function (16) with the solution

$$\alpha_0^*(\lambda) = \tau_0^{-1}\left[\sqrt{1 + \tilde{\gamma}^2\lambda(1-\lambda)} - 1\right] \qquad (17)$$

obtained in Ref. [20] based on the entropy production rate in Eq. (13) with fixed center of mass ($\mathbf{R} = 0$), which also fulfills a fluctuation theorem. Note that our expression for $h(\sigma)$ based on Eq. (16) predicts substantially larger fluctuations especially for trajectories with larger than mean entropy production.

The dumbbell just discussed also provides a counterexample to the standard definition of nonequilibrium. In pure rotational flow with skew-symmetric matrix

$$\boldsymbol{\kappa} = \boldsymbol{\kappa}^\mathrm{A} = \begin{pmatrix} 0 & \dot{\gamma}/2 \\ -\dot{\gamma}/2 & 0 \end{pmatrix},$$

there is a nonvanishing current manifested through the ever tumbling dumbbell superficially indicating nonequilibrium. On the other hand, the length $|\mathbf{r}|$ undergoes only equilibrium fluctuations. For all practical purposes, this is an equilibrium system. In fact, the applied power (2) vanishes. Combining this result with the moving trap case discussed at the beginning, we conclude that in the presence of flow the proper frame-invariant criterion for distinguishing equilibrium from genuine nonequilibrium is whether or not the applied power obeys $\dot{w} = 0$.

Summarizing further, we have shown that considering external flow in the expression for the work (2) [and therefore in the derived quantities like dissipated heat (3) and entropy production (6)] guarantees frame invariance of stochastic thermodynamics. While formally two expressions for the asymmetric part of the path probability under time reversal are possible which both fulfill the fluctuation theorem, only one leads to a consistent identification of thermodynamic quantities for the dynamics of soft matter systems in flow.

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